CHEMICAL INVESTIGATION OF TWO ANCIENT BRONZE STATUETTES FOUND IN GREECE[1]

EARLE R. CALEY
Department of Chemistry,
The Ohio State University,
Columbus, Ohio

A great deal is known about Greek and Roman statuary bronzes from the standpoint of art, but very little is known about them from the standpoint of chemical composition. Only a few analyses have been made, and most of these are analyses of objects of uncertain or unknown provenance. Our information concerning the composition of Greek statuary bronze is especially meager. By a fortunate chance several bronze objects and fragments of bronze objects were found about fifteen years ago in the filling of an abandoned ancient well in the Agora, or ancient market place, at Athens, Greece, and two of the objects, both of them statuettes, were given to the author for chemical investigation after attempts at restoration were unsuccessful. The archaeological evidence, such as the coins found in the filling of the well, showed that these statuettes had been dropped or thrown in the well at about the end of the second century A. D., so that their immediate provenance is very definitely established. One of the statuettes was a female figure about 10 cm. high, and the other was the figure of an animal, probably a stag, about 6 cm. long and 4.5 cm. high. Both were badly corroded, but each contained a substantial core of essentially uncorroded metal from which samples suitable for microscopic examination and chemical analysis could be taken.

MICROSCOPIC EXAMINATION

Both unetched and etched specimens of metal from both statuettes were examined microscopically by Miss Virginia Sheipline, a senior student in chemistry, to whom the author is indebted for the accompanying photomicrographs. Although specimens of polished but unetched metal from the female statuette appeared to be clean and solid to the unaided eye, the presence of numerous cavities and inclusions was readily apparent on sufficient magnification (Fig. 1). Some of the dark spots that appear in the photomicrograph represent minute cavities or blowholes which were evidently formed in the metal at the time of manufacture. Some of the others apparently represent nonmetallic impurities trapped in the molten metal during solidification. Still others probably represent places where intergranular corrosion has occurred in the course of long burial. After etching with a very dilute mixture of hydrochloric and nitric acids the metal of this statuette was seen to have a peculiar, coarse, dendritic structure (Fig. 2). After etching with an alcoholic solution of ferric chloride containing hydrochloric acid the dendrites had the normal appearance of those in an ordinary cast tin bronze, but the structure was not so easy to photograph because of lack of contrast. The undisturbed dendritic structure showed clearly that the statuette was produced solely by casting. The presence of a great number of globular and irregular particles of metallic lead, varying greatly in shape and size, was apparent in the polished but unetched metal from the animal statuette (Fig. 3). It is evident that the metal contained a very high proportion of unalloyed lead. The metal surrounding the lead, after etching with ammonium persulfate and hydrogen peroxide solution, had a dendritic structure (Fig. 4). Because of its very high lead content, the metal of this statuette was very difficult to etch properly for the purpose of preparing a photo-

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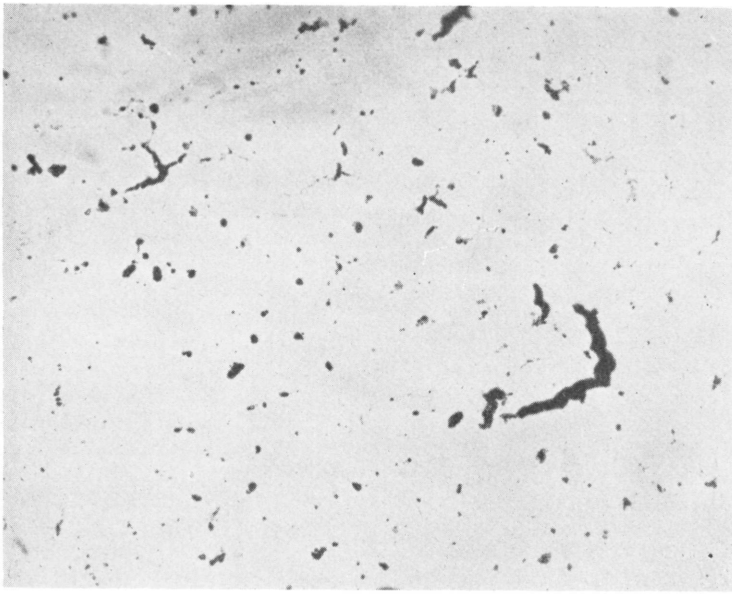

FIG. 1. Photomicrograph of polished but unetched section of metal from female statuette. 150 ×.

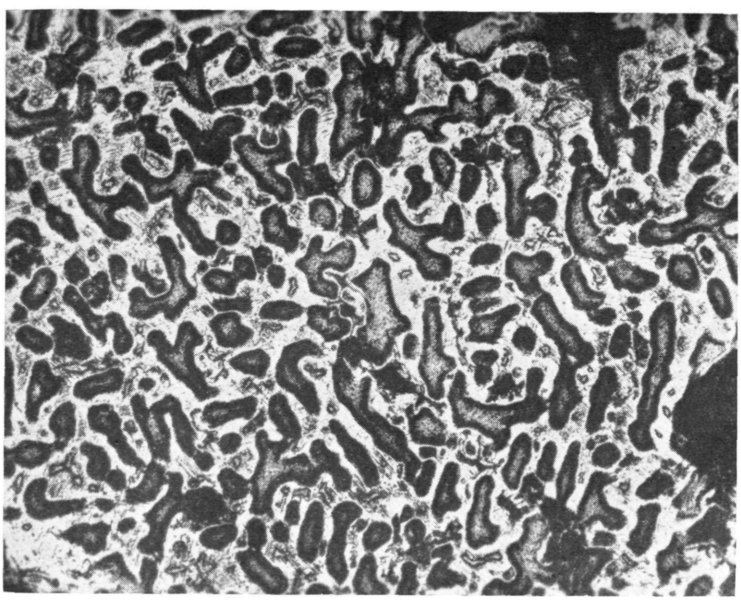

FIG. 2. Photomicrograph of etched section of metal from female statuette. 150 ×.

graph, and the dendritic structure in Fig. 4 is not very distinct. However, under the microscope it could be seen that the dendrites were often arranged radially around the larger lead globules and that the lead itself had a coarse crystalline structure. The generally globular shape of the lead particles and the dendritic structure of the matrix showed clearly that this statutte had also been produced solely by casting.

METHOD OF CHEMICAL ANALYSIS

Accurately weighed samples of about a gram were treated with nitric acid for the separation of the tin. After evaporation of the solution to small volume, followed by dilution and digestion, the hydrated tin oxide was filtered off on quantitative paper, washed with hot dilute nitric acid, and ignited to constant weight in an electric muffle furnace. As no pink or purple coloration of the tin oxide was observed in the course of this separation, provision for the separation and determination of gold was not necessary. For the determination of the true percentages of tin, the ignited residues of impure tin oxide were treated with ammonium iodide according to the method of Caley and Burford.[2] The filtrates from the separation of the tin were treated with dilute hydrochloric acid to detect silver. This metal was found to be present in one of the bronzes, and it was separated by adding sufficient hydrochloric acid to precipitate all the silver as the chloride. The precipitates of silver chloride were collected in filter crucibles, washed with dilute nitric acid, and dried in an oven to constant weight. To these filtrates, as well as to those which gave no reaction for silver, the proper volume of concentrated sulfuric acid was added, and after evaporation, dilution, and digestion, the separated lead sulfate was collected in filter crucibles, washed with cold, very dilute sulfuric acid, dried, ignited and weighed. The filtrates from the separation of the lead were electrolyzed, using a platinum gauze anode and cathode. Usually a small amount of lead dioxide deposited on the anode. This was calculated to metallic lead and this weight was added to the weight of the lead found by the sulfate determination so as to give the total amount of lead in each sample. Copper was found from the increase in the weight of the cathode. The filtrates from the electrolytic determinations were evaporated to small volume, and iron was precipitated by the addition of ammonium hydroxide solution. The hydrated iron oxide was filtered off on quantitative paper, ignited and weighed as ferric oxide, from which the weight of iron was calculated. Nickel was determined in the filtrates by precipitation with a solution of dimethylglyoxime, the nickel compound being collected in filter crucibles, washed with water, and dried to constant weight in an oven. After the destruction of the excess of dimethylglyoxime in the filtrates from the nickel determination by evaporation with nitric acid, zinc was precipitated as phosphate in neutral solution by the addition of secondary ammonium phosphate. The precipitates were collected in filter crucibles, washed, dried in an oven, and weighed as zinc ammonium phosphate. Separate samples were examined for arsenic and sulfur but neither of these elements could be detected. This is merely an outline of the method of analysis, many necessary manipulative details being omitted for the sake of brevity.

ANALYSTS AND RESULTS OF ANALYSES

The analyses were made under the direction of the author by Miss Virginia Sheipline and Messrs. W. H. Deebel and N. V. Lovegren. Miss Sheipline analyzed two samples of metal taken from the animal statuette and Mr. Deebel two from the female statuette. Mr. Lovegren analyzed three samples taken from the female statuette and one from the animal statuette. The results shown in Table I are weighted averages from all these analyses. In addition to the elements listed in the table, a small proportion of oxygen was also present in the

[2]Caley, E. R., and Burford, M. G., *Ind. Eng. Chem., Anal. Ed.*, 8, 114–118 (1936).

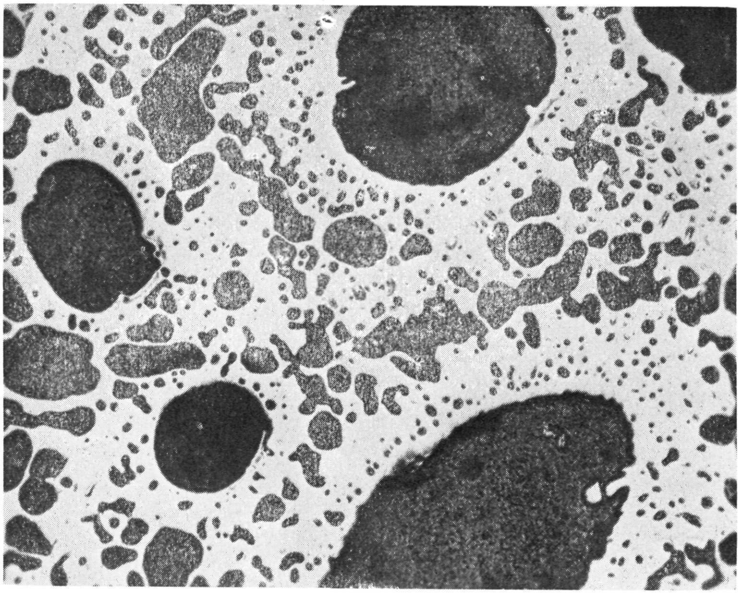

FIG. 3. Photomicrograph of polished but unetched section of metal from animal statuette. 150 ×.

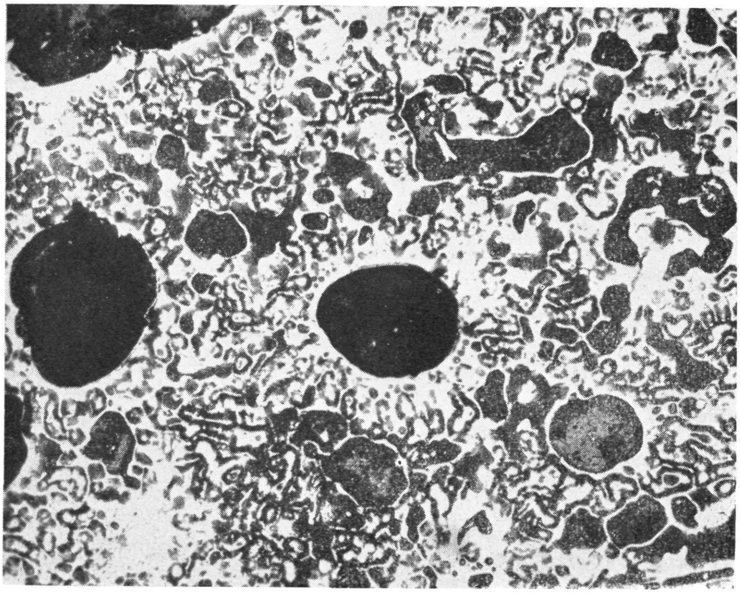

FIG. 4. Photomicrograph of etched section of metal from animal statuette. 150 ×.

form of metallic oxides as shown by the microscopic examination, but no attempt was made to determine this quantitatively.

DISCUSSION OF ANALYTICAL RESULTS

The analysis shows that the metal of the female statuette is an ordinary bronze of moderate tin content containing various impurities commonly found in ancient bronzes. On the other hand, the metal of the animal statuette is an alloy of low tin content and extraordinarily high lead content. In the metal of the female statuette the lead must be regarded as a mere accidental impurity, but in the other it is certainly an intentional component of the alloy. The small proportion of silver in the metal of the animal statuette is in all probability an accidental impurity accompanying the lead. The great difference in the proportions of tin and lead in the metal of the two statuettes is the most striking and significant result of these analyses.

A comparison of the present analyses with previous analyses of statuary bronzes of the classical period brings out some interesting relationships. In Table II are shown, with one exception, all the previous analyses of Greek statuary bronzes that could be located. The one omitted from the table appeared to be unreliable because of the low summation of the analytical results. It will be noted that in these bronzes copper and tin are the only main components and that lead is absent. The apparent absence of such usual impurities as iron and nickel from the

TABLE I

ANALYSIS OF SAMPLES OF METAL FROM THE STATUETTES

Component	Female Figure	Animal Figure
Cu	92.28	60.40
Sn	7.00	3.74
Pb	0.13	34.56
Ag	none	0.22
Fe	0.16	0.33
Ni	0.05	0.09
Zn	0.22	0.40
Au, As, S	none	none
Total	99.84	99.74

first two analyses of Table II is, in all probability, due to the approximate analytical methods that were used. In Table III are shown all the previous reliable analyses of Roman statuary bronzes that could be located. It will be noted that in these bronzes the proportion of tin is generally much lower than in the Greek bronzes of Table II and that lead is always present in considerable proportion. In most of them it exceeds the proportion of tin and must be regarded as an intentional major component. The presence of lead in relatively high proportion appears to be characteristic of Roman statuary bronzes. In addition to this experimental evidence there is literary evidence for lead as an intentional component in Roman statuary bronze, for Pliny,[3] in giving formulas for the composition of the bronze used for statuary, lists lead as a necessary ingredient in all of them.

KEY TO OBJECTS AND ANALYSTS

A. Fragment of statue found in Antikythera. Date about third century B. C. Analysis by Rhousopoulos. Published in Diergart, Beiträge aus der Geschichte der Chemie dem Gedächtnis von Georg W. A. Kahlbaum, Leipzig and Vienna, 1909, p. 187.

[3]Natural History, Book XXXIV, secs. 97–98.

B. Female statue or statuette of fine style. Provenance unknown. Analysis by Göbel. Published in his work, Ueber den Einfluss der Chemie auf die Ermittelung der Völker der Vorzeit oder Resultate der chemischen Untersuchung metallischer Alterthümer, Erlangen, 1842, p. 23.
C. Female statuette. Provenance unknown. Analysis by Bibra. Published in his work, Die Bronzen und Kupferlegirungen der alten und ältesten Völker mit Rucksichtnahme auf jene der Neuzeit, Erlangen, 1869, pp. 88–89.
D. Fragment of statuette. Provenance unknown. Analysis by Bibra, *loc. cit.*

TABLE II

Previous Analyses of Greek Statuary Bronzes

Object	Cu	Sn	Pb	Fe	Ni	Zn	Ag	Sb	S
A	84.74	14.29	....	....	....	....	....	....	....
B	88.54	11.46	....	....	....	....	....	....	....
C	88.51	10.13	none	1.02	0.34	none	tr.	tr.	tr.
D	89.96	9.22	none	0.44	0.38	none	none	tr.	none

TABLE III

Analyses of Roman Statuary Bronzes

Object	Cu	Sn	Pb	Fe	Ni	Zn	Ag	Sb	S
A	80.70	9.44	7.68	....	....	1.92	....	....	....
B	81.23	9.33	9.34	0.10	....	....	....	....	....
C	78.77	9.03	12.07	0.13	tr.	none	none	tr.	tr.
D	72.63	8.19	19.01	0.17	....	....	....	....	....
E	80.65	8.13	10.00	0.30	0.17	0.75	none	none	none
F	76.03	7.33	12.11	1.20	0.20	3.03	tr.	tr.	0.10
G	68.62	6.77	24.46	0.13	....	....	0.02	....	....
H	87.36	6.23	6.20	tr.	0.21	tr.	none	none	none
I	85.64	4.22	9.13	0.80	0.20	tr.	none	none	0.01

KEY TO OBJECTS AND ANALYSTS

A. Statue found at Brescia. Unknown date. Analysis by Arnaudon. Published in *Bull. soc. chim.* 1, 245 (1860).
B. Base of a statue found at Bern. Unknown date. Analysis by Fellenberg. Quoted by Bibra, Die Bronzen und Kupferlegirungen der alten und ältesten Völker mit Rücksichtnahme auf jene der Neuzeit, Erlangen, 1869, pp. 72–73.
C. Statuette of Minerva. Provenance unknown. Analysis by Bibra, *loc. cit.*
D. Statue. Provenance uncertain. Analysis by Fellenberg. Quoted by Bibra, *loc. cit.*
E. Statuette. Provenance unknown. Analysis by Bibra, *loc. cit.*
F. Statuette of Victory. Provenance unknown. Analysis by Bibra, *loc. cit.*
G. Base of statue found at Bern. Unknown date. Analysis by Fellenberg. Quoted by Bibra, *loc. cit.*
H. Statuette of an animal. Provenance unknown. Analysis by Bibra, *loc. cit.*
I. Statuette. Provenance unknown. Analysis by Bibra, *loc. cit.*

This sharp difference between the composition of Greek statuary bronze and Roman statuary bronze is paralleled by a similar difference between the composition of Greek coinage bronze and Roman coinage bronze. Of special interest for the present study is the difference in the composition of the coinage bronze of Athens in Greek and Roman times. The series of typical analyses shown in Table IV were selected from the author's memoir on the composition of ancient

Greek bronze coins.[4] From this table it will be seen that the tin content of the coins of Greek times is invariably higher than in the coins struck in Roman times, and that the lead content is invariably lower. In most of the coins of Greek times, lead is either absent entirely or is present in such small amount that it must be considered an accidental impurity. Only in a small proportion of the coins, as in Nos. 5, 10, and 16 of Table IV, does it appear in high enough amount to be considered an intentional component. In the coins of Roman times it is clearly an intentional component just as in Roman statuary bronze. Lead is also found as a major component in other kinds of Roman bronze objects. Thus it appears to be true in general that Greek bronze is characterized by a relatively high tin content and the presence of little or no lead, and Roman bronze by a relatively low tin content and a high lead content.

TABLE IV

Proportions of Major Components in Athenian Coinage Bronzes

No.	Period	Cu	Sn	Pb
1	Third Century B. C.	87.99	12.05	none
2	" " "	87.06	11.32	1.51
3	" " "	87.49	10.67	1.29
4	" " "	89.64	10.40	0.01
5	" " "	83.57	10.24	5.70
6	" " "	86.01	10.08	3.18
7	" " "	90.04	9.93	none
8	" " "	88.81	9.80	1.36
9	" " "	89.54	9.40	0.54
10	" " "	83.88	9.20	6.38
11	" " "	88.79	8.55	2.56
12	" " "	90.30	8.25	1.28
13	Second Century B. C.	88.74	11.10	0.22
14	" " "	89.03	10.60	0.20
15	" " "	86.38	10.56	2.73
16	" " "	84.96	9.89	5.15
17	First Century B.C.	78.21	7.56	13.26
18	" " "	71.23	6.84	20.38
19	First Century A. D.	70.55	5.93	23.03
20	First or Second Century A. D.	68.05	4.45	26.82
21	Second Century A. D.	63.23	3.89	32.51
22	Second or Third Century A. D.	66.05	4.10	29.32
23	Third Century A. D.	66.19	3.75	29.18

Now if the analyses of Table I are compared with those in Tables II, III, and IV the obvious conclusion seems to be that the animal statuette found in Athens was a product of Roman times and that the female statuette was a product of Greek times. The animal statuette could have been made only a few years before it was deposited in the well, and at the most was probably made less than two centuries before. On the other hand, the female statuette was probably made at least three centuries before it was deposited and could have been made five or six centuries before. On the basis of the archaeological evidence alone, there was no reason to suspect that these two statuettes, which were found together, were not products of the same period, but the chemical evidence strongly indicates, even if it does not definitely prove, that they were products of different periods. This is another example of how the chemical investigation of ancient objects may yield new information about them that may correct or supplement the information derived from the archaeological evidence.

[4]Caley, E. R. The Composition of Ancient Greek Bronze Coins. Philadelphia, 1939.